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Double Layer Structure and Electrode Processes.

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DOUBLE LAYER STRUCTURE
AND
ELECTRODE PROCESSES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

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ABSTRACT

The influence of the double layer structure on electrochemical kinetics is discussed for simple processes without specific adsorption and for processes with coupled chemical reaction. The influence of both the electrolyte concentration and the nature of the electrode is analyzed. Interpretation of processes without chemical reaction is based in two fundamental ideas (Frumkin): a) the double layer structure influences the effective difference of potential which favors the forward electrochemical reaction and hinders the backwards reaction: b) because of electrostatic interactions the effective concentrations of reactants in the double layer are different from the bulk concentrations.

The influence of electrolyte concentration was studied for the reduction of iodate ions in alkaline solution on a dropping mercury electrode. The influence of the nature of the electrode was studied for the reduction of bromate ions in alkaline solution and the exchange current of the couple $\text{Cr}(\text{CN})_6^{-3} + e \rightleftharpoons \text{Cr}(\text{CN})_6^{-4}$ in cyanide solution at a dropping mercury electrode and three thallium amalgams of different thallium concentrations. The influence of the electrolyte and the nature of the electrode was considered in the reduction of chromate ion in alkaline solution. Agreement with theory is satisfactory.

Double layer effects for processes with a coupled chemical reaction are explained by variation of the concentration of reactants in the reaction layer. Approximate correction for this variation is possible with a simple treatment when the thickness of the reaction layer is small in comparison with that of the double layer. Results are given for the single pulse galvanostatic method. A more general treatment developed by Matsuda is applied to polarographic waves obtained in the discharge of cadmium cyanide complexes on mercury and three thallium amalgams of different thallium concentrations. Theory and experiment are only in qualitative agreement presumably because of the occurrence of more than one chemical step.

Implications of the very significant role of the double layer in electrochemical kinetics are discussed.

CHAPTER I

INTRODUCTION

Double layers are established at the boundary between two phases because of redistribution of electrical charges or dipole orientation in the vicinity of the interface. Hence there is an excess of positive charges on one side and an excess of negative charges on the other side of the boundary. This work is restricted to the boundary between a metallic conductor and an electrolytic solution, and the expression electrical double layer designates that region between the surface of the electrode and the bulk of the solution.

The structure of the electrical double layer is important in electrochemical kinetics for at least two reasons. (a) It influences the effective difference of potentials which favors the electrochemical reaction in one direction and hinders it in the opposite direction. (b) The effective concentration of reacting species, particularly in the case of ions, are different from the bulk concentrations because of the double layer structure, and the rate of the electrode reaction is affected accordingly. The study of these two effects was progressively developed by Frumkin and his school mostly for the reduction of hydrogen ions (1-3), the electrolytic oxidation of hydrogen (4), the reduction of anions (5), the reduction of oxygen (6) and adsorption processes (7).

A few other authors, and particularly Gierst (8,9) also considered the structure of the double layer in the correlation with electrode kinetics. (Cf. detailed bibliography in a recent paper from this laboratory (10).)

Scope and Purpose of this Work.

Two cases can be distinguished in double layer effects according to whether or not there is specific adsorption. An electrolyte is said to be specifically adsorbed at an electrode surface when the coordinates of the electrocapillary maximum are a function of the concentration of this electrolyte. Adsorption is the stronger the smaller the repulsion by the electrode, and it generally becomes quite negligible at sufficiently positive or negative potentials with respect to the point of zero charge. In addition to the foregoing two cases, double layer effects may have to be considered in electrode processes which are preceded or followed by a chemical reaction.

The structure of the double layer can be modified by a change in the nature and/or the concentration of the supporting electrolyte, or by a change in the nature of the electrode. Both methods will be considered in this work for different possible processes. The influence of the nature of the electrolyte was studied with a dropping mercury electrode, and that of the nature of the electrode with dropping thallium amalgams of different thallium concentrations. Both types of electrodes have the advantage of a continuously renewed surface with minimum contamination by impurities from the solu-

tion. Contamination by traces of adsorbed organic substances must be avoided in this work because of the resulting change in the double layer structure.

Survey of Theories of the Double Layer (11-13).

The first model of the electrical double layer was introduced by Helmholtz (1881), who regarded it as a parallel plate condenser. This model proved to be incorrect since it predicted a constant capacity, whereas it is found experimentally that the capacity of the double layer varies with potential.

Gouy (1910) suggested that the electrical forces which are responsible for the existence of the double layer are in equilibrium with the osmotic forces which tend to maintain homogeneity. Hence the ions could not be concentrated at a definite distance from the surface of the electrode as required by Helmholtz' model, but their concentration should gradually increase or decrease with distance according to their sign and the sign of the charge of the electrode surface.

Gouy, and independently, Chapman (1913), applied Poisson's equation to find the equilibrium distribution of the ions in such a diffuse double layer. (It is interesting that his mathematical analysis was very similar to that of Debye and Hückel for the distribution of ions in the "ionic atmosphere" round any given ion in a dilute solution of an electrolyte). The analysis of Gouy and Chapman predicted a value for the capacity of the double layer which was about an order of mag-

nitude too high. (A typical experimental value is 20 microfarads per cm^2 for liquid mercury in a solution of a non-adsorbed electrolyte). This discrepancy led Stern (1924) to propose for the double layer a model composed of two regions, one of which, in contact with the electrode, has the properties of the Helmholtz layer and the other is a diffuse double layer.

The combination of the ideas of Helmholtz, Gouy, Chapman and Stern is the basis of our modern concepts of the double layer structure.

CHAPTER II

SIMPLE ELECTRODE PROCESSES WITHOUT SPECIFIC ADSORPTION

FUNDAMENTALS

Current-Potential Characteristics.

The model of Fig. 1 for the double layer is satisfactory in the absence of specific adsorption. The double layer is composed of two parts: the diffuse double layer and the Helmholtz double layer between the metal and the plane of closest approach. The structure of the double layer has an influence on the current-potential characteristic for an electrode process involving a single rate determining step for two reasons: (a) the effective concentrations of reacting species must be taken in the plane of closest approach, and (b) the differences of potentials, $\phi_H - \phi_S^*$, must be subtracted from the electrode potential. Cathodic reactions involving a rate-determining step with n_a electrons will be considered here because fundamental results can be expressed with a minimum of algebra. The more complicated case of fast reactions is treated below. Thus, one has for the cathodic current density (a similar

*The difference $\phi_H - \phi_S$ is noted as ψ in the Russian literature, and the electrode potential or the difference between the electrode potential and the potential at the point of zero charge are designated by φ . These notations are not used here because ψ and ϕ (not φ) generally designate outer and inner potentials, respectively.

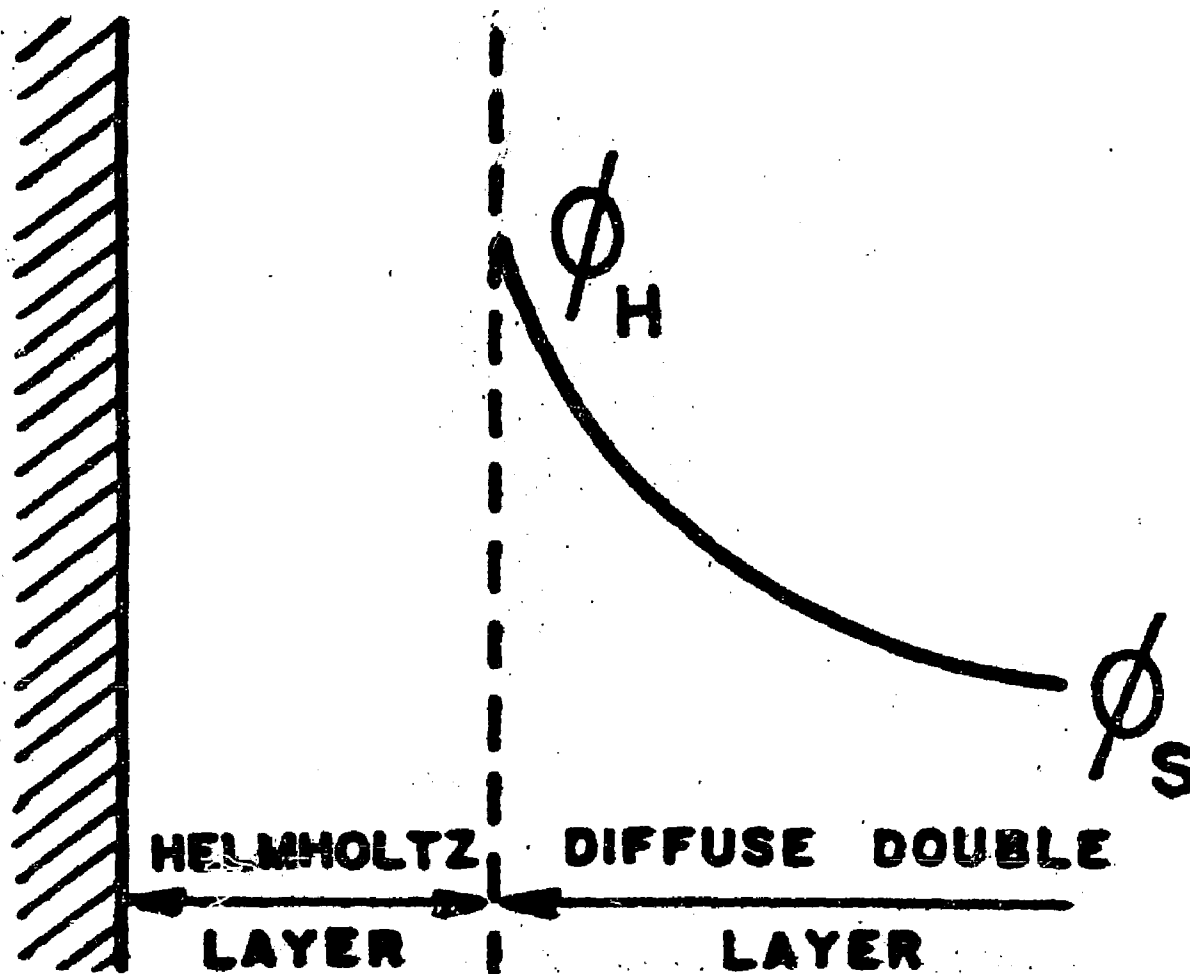


Fig. 1.- Model for the double layer at a metal-electrolyte interface in absence of specific adsorption

equation can be written for the backward reaction):

$$I = kC^* \exp \left[- \frac{\alpha n_a F E}{RT} \right] \exp \left[\frac{\alpha n_a F (\phi_H - \phi_S)}{RT} \right] \quad (\text{II-1})$$

where k is a proportionality constant, C^* is the concentration of reactant in the Helmholtz plane, α the transfer coefficient, E the usual electrode potential (European convention), and R , T , and F have their usual significance.

Note that the potential E is not referred to the point of zero charge E_z in equation II-1. In the absence of specific adsorption E_z is independent of the electrolyte concentration and the introduction of E_z offers no particular advantage. In the case of specific adsorption, the current still varies exponentially with potential as a first approximation but equation II-1 is not applicable, and an interpretation based on the shift of the point of zero charge with electrolyte concentration may be open to question as was pointed out recently (10).

For an ion of valence z , the concentration C^* of reactants in the Helmholtz plane is

$$C^* = C_s \exp \left[- \frac{zF(\phi_H - \phi_S)}{RT} \right] \quad (\text{II-2})$$

where z is taken with its sign and C_s is the concentration outside the double layer (more rigorously in the region of solution where variations of concentration due to the double layer structure become negligible). If the reactant is a neutral species which is not adsorbed one has approximately $C^* \approx C_s$. Variations of the concentration of a neutral sub-

stance resulting from the electrical field in the double layer could be treated, in principle, on a thermodynamic basis (14), the electrical field strength being calculated from double layer theory. This effect will not be considered here.

It follows from equations II-1 and II-2 that, at constant current density, the shift ΔE in electrode potential corresponding to a change $\Delta(\phi_H - \phi_S)$ is

$$\Delta E = \frac{(\alpha n_a - z)}{\alpha n_a} \Delta(\phi_H - \phi_S) \quad (\text{II-3})$$

if α is constant. If $z=0$, $\Delta E = \Delta(\phi_H - \phi_S)$, and the change of potential is entirely caused by variation of the difference of potentials across the diffuse double layer.

If α varies, one has at constant current density

$$(\alpha E - \alpha' E') n_a = (\alpha n_a - z)(\phi_H - \phi_S)_E - (\alpha' n_a - z)(\phi_H - \phi_S)_{E'} \quad (\text{II-4})$$

and the shift of potential is readily obtained.

Equations II-3 and II-4 also give the shift of half-wave potential for irreversible polarographic waves provided that the diffusion current does not vary appreciably (constant current density at $E_{\frac{1}{2}}$) upon variation of the electrolyte concentration.

Equation II-1 shows that at constant $(\phi_H - \phi_S)$ a plot of $\log I$ versus E gives the product αn_a , provided there is no concentration polarization. It is seen from equations II-1 and II-2 that a plot of $(\phi_H - \phi_S)$ versus $\log I$ (at constant E) gives the value of $\alpha n_a - z$, from which z can be found.

Calculation of $(\phi_H - \phi_S)$

The difference $(\phi_H - \phi_S)$ is such that the sum of the charges on the metal and in the diffuse double layer is equal to zero.

Thus,

$$K_i \left[(E - E_Z) - (\phi_H - \phi_S) \right] = \left[\frac{RT}{2\pi} \sum C_i^S \left[\exp \left(- \frac{z_i F (\phi_H - \phi_S)}{RT} \right) - 1 \right] \right]^{1/2} \quad (\text{II-5})$$

Where K_i is the integral capacity of the Helmholtz double layer, E_Z the electrode potential at the point of zero charge, ϵ the dielectric constant* (assumed to be constant in the double layer), and C_i the bulk concentration of ion i of valence z_i (with its sign) in moles. cm^{-3} . The right hand member in equation II-5 is taken from the classical Gouy-Chapman theory.

If only z-z electrolytes are present, equation II-5 reduces to

$$K_i \left[(E - E_Z) - (\phi_H - \phi_S) \right] = \left(\frac{2RT\epsilon C_t}{\pi} \right)^{1/2} \sinh \left[\frac{|z| F (\phi_H - \phi_S)}{2RT} \right] \quad (\text{II-6})$$

Where $|z|$ is now taken in absolute value, and C_t is the sum of the electrolyte concentrations.

Variations of $(\phi_H - \phi_S)$ with $E - E_Z$ are shown in Fig. 2 for different molar concentrations of a 1-1 electrolyte and for the constant value, $K_i = 20$ microfarads. cm^{-2} (K_i actually varies somewhat with E in the range considered.) A similar diagram is given by Frumkin et al (17).

It is seen from Fig. 2 that one can easily change $(\phi_H - \phi_S)$ by 0.1 volt by variation of the electrolyte concentration,

* Saturation of the dielectric can be neglected as a first approximation.

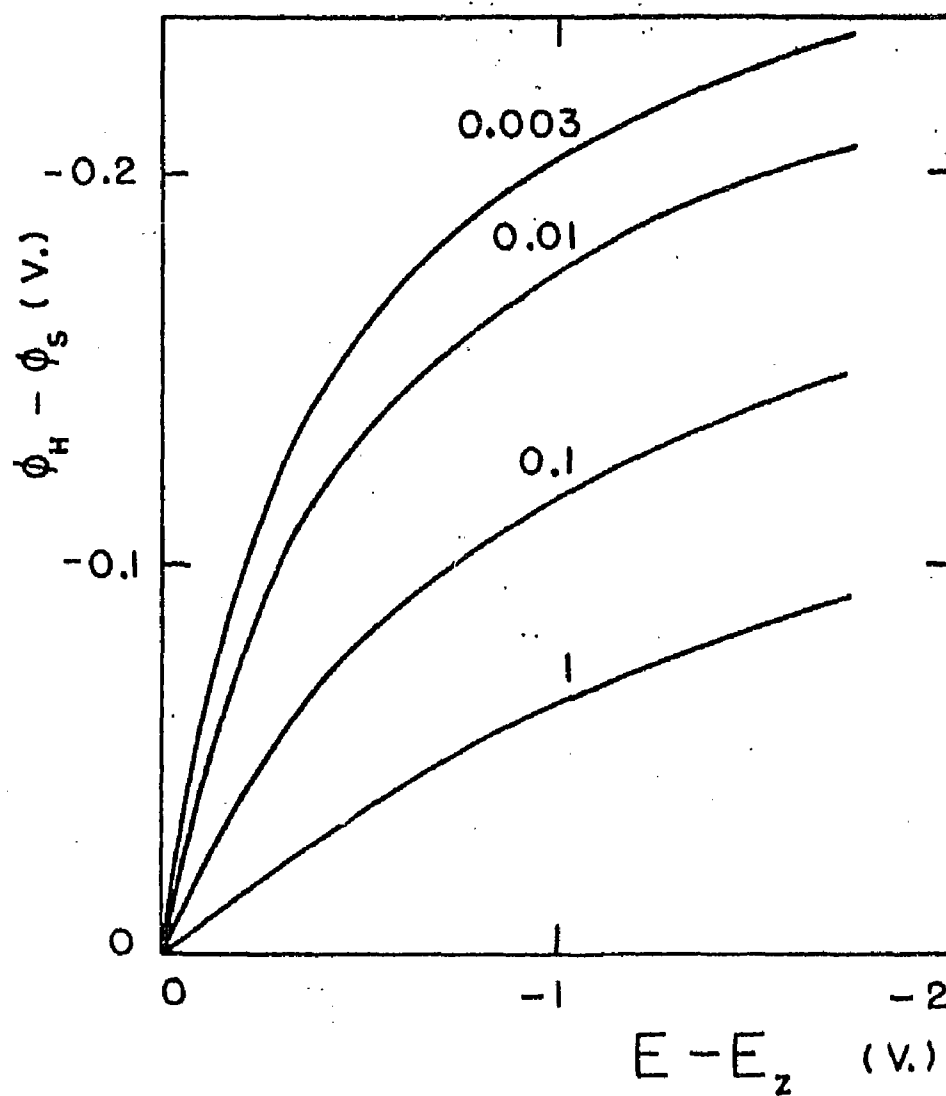


Fig. 2.- Variations of $\phi_H - \phi_S$ with $E - E_z$ for different molar concentration of a 1-1 electrolyte

and consequently the change ΔE of equation II-3 can be quite pronounced.

When $|\phi_H - \phi_S| \ll |E - E_z|$, i.e. at potentials not near the point of zero charge, and $|\phi_H - \phi_S| > 0.05$ volt, equation II-6 yields approximately for a given E

$$\phi_H - \phi_S = \pm \frac{RT}{|z|F} \ln C_t + \text{constant} \quad (\text{II-7})$$

where the constant can be written in an explicit form from equation II-6, and the positive and negative signs hold, respectively, for the cathodic and anodic ranges of potentials as referred to the point of zero charge. Equation II-7 is useful because it readily gives the dependence of $\phi_H - \phi_S$ on C_t , but the more rigorous equation II-6 or equation II-5 for $z-z'$ electrolytes must generally be applied.

Exchange Current in the Absence of Specific Adsorption.

The exchange current will be derived for processes of the type $O + ne \rightleftharpoons R$ where O and R are soluble species. The derivation follows the one previously given by Berzins and Delahay (16) except that correction for the double layer is now introduced for processes without specific adsorption.

If $n = n_a$ (see equation II-1), the current density for a net cathodic process may be calculated according to the equation

$$I = nF \left\{ \begin{array}{l} C_O k_f^0 \exp\left[-\frac{\alpha n F E}{RT}\right] \exp\left[\frac{F(\alpha n - z_O)(\phi_H - \phi_S)}{RT}\right] \\ - C_R k_b^0 \exp\left[\frac{(1-\alpha) n F E}{RT}\right] \exp\left[-\frac{F[(1-\alpha)n + z_R](\phi_H - \phi_S)}{RT}\right] \end{array} \right\} \quad (\text{II-8})$$

where C_O and C_R are the concentrations in the region of solution where variations of concentration due to the double layer structure (not due to concentration polarization) can be neglected; the k^0 's are rate constants at some reference potential, for instance at $E=0$ volt versus the normal hydrogen electrode; and the z 's are the valences of O and R.

At the equilibrium potential, $E=E_e$, $I=0$ and there is no concentration polarization. Hence, $C_O=C_O^0$ and $C_R=C_R^0$, where the C^0 's are the bulk concentrations. By noting that $C_O^0/C_R^0 = \exp(nF/RT)(E_e-E^0)$, where E^0 is the formal potential for $O + ne = R$, one can write the quantity

$$nFC_O^0 k_f^0 \exp\left[-\frac{\alpha nFE_e}{RT}\right] \exp\left[\frac{(\alpha n-z_O)F(\phi_H-\phi_S)}{RT}\right]$$

in the form

$$I_0 = nFC_O^0 (1-\alpha) C_R^0 \alpha k_s \exp\left[\frac{(\alpha n-z_O)F(\phi_H-\phi_S)}{RT}\right] \quad (\text{II-9})$$

with k_s , the rate constant at the formal potential E^0 , given by

$$k_s = k_f^0 \exp(\alpha nFE^0/RT) = k_b^0 \exp[(1-\alpha)nFE^0/RT] \quad (\text{II-10})$$

The exchange current density I_0 can also be written in terms of only C_O^0 or C_R^0 by noting that $C_O^0/C_R^0 = \exp(nF/RT)(E_e-E^0)$.

The current-potential characteristic

$$I = I_0 \left\{ \begin{array}{l} \frac{C_O}{C_O^0} \exp\left[-\frac{\alpha nF(E-E_e)}{RT}\right] \\ - \frac{C_R}{C_R^0} \exp\left[\frac{(1-\alpha)nF(E-E_e)}{RT}\right] \end{array} \right\} \quad (\text{II-11})$$

has the same form as the one derived without consideration of double layer effects except that the exchange current density I_0 now depends on the double layer structure because of the term in $\phi_H - \phi_S$. This term should account for the salt effect in the absence of specific adsorption in the absence of kinetic complications or marked departure from the model used in these calculations. Values of k_s should be corrected accordingly.

Non-Equilibrium Double Layer.

In the foregoing treatment it was assumed that the electrochemical reaction does not change the double layer from its equilibrium structure. This can be considered to be true if $\phi_H - \phi_S$ and the current are not large. For large currents and large $\phi_H - \phi_S$ however, the electrostatic equilibrium is disturbed and we have a "dynamic $\phi_H - \phi_S$ effect", the theory for which was developed by Levich (17). It was pointed out by Frumkin (5) that this effect becomes important only at very low concentrations of inert electrolyte (about 10^{-4} molar or less), and for the purposes of this work it can be disregarded.

CHAPTER III
ELECTRODE PROCESSES
WITH COUPLED CHEMICAL REACTION

Simple Interpretation and its Application to the Single Pulse Galvanostatic Method (10).

Processes in which the electrochemical reaction is preceded or followed by a chemical reaction will be considered. Except for Gierst (8,9)* the double layer structure has not been considered in previous analysis of such processes and it has generally been implicitly assumed that the concentrations are independent of the distance from the electrode before electrolysis. A rigorous treatment of these processes considering the structure of the double layer is rather involved but experimental data presumably can be explained by a simple interpretation developed on the assumption that the double layer thickness is either small or large in comparison with the reaction layer thickness. In the first case there is hardly any double layer effect; in the second case there is a definite effect.

Only results for the current step method will be discussed because of their direct verification from existing data. Extension to the potentiostatic method and to polarography

*The following analysis was developed independently of Gierst.

is immediate.

Consider the reaction $Z \rightleftharpoons O + ne = R$ in which Z is not reduced or oxidized, and assume that the conditions of the single-pulse galvanostatic method prevail. The transition time τ_k is such that (18)

$$I\tau_k^{\frac{1}{2}} = I\tau_d^{\frac{1}{2}} - \frac{\tau_d^{\frac{1}{2}}}{2K(k_f + k_b)^{\frac{1}{2}}} I \quad (\text{III-1})$$

where k_f and k_b are the formal rate constants for $Z \rightleftharpoons O$; I is the current density; K the equilibrium constant for the chemical reaction; and τ_d the transition time that would be measured if Z were reduced directly, all other conditions being the same. The product $I\tau_d^{\frac{1}{2}}$ is independent of current density. It follows from equation III-1 that a plot of $I\tau_k^{\frac{1}{2}}$ against I is linear. Thus the formal rate constants k_f and k_b can be deduced from this plot provided that K is known.

An equation of the same form as III-1 can be derived on the assumption that the chemical reaction occurs in a layer of thickness μ . By comparison of the resulting equation with III-1 one deduces $\mu = \sqrt{\frac{D}{k_b}}$, D being the common value of the diffusion coefficients for Z and O (assumed to be equal). For example $\mu = 2 \times 10^{-7}$ cm. for $D = 5 \times 10^{-6}$ cm² sec⁻¹ and $k_b = 10^8$ sec⁻¹. The thickness of the diffuse double layer is somewhat larger than this value of μ , at least for fairly dilute electrolytes. In the absence of specific adsorption, one can then assume, as a first approximation, that the reaction $Z \rightleftharpoons O$ occurs mostly in a layer in which concentrations of ions can be corrected on the basis of equation

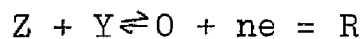
(II-2). The salt effect on the kinetics of the reaction proper (variation of activities) is neglected.

By noting that the formal k 's in equation (III-1) are the products of rate constants k by the Boltzman factor in equation (II-2) one obtains for the slope of the $I\tau_k^{\frac{1}{2}}$ versus I line

$$\theta = - \frac{\pi^{\frac{1}{2}}}{2K \left\{ k_f^1 \exp\left[-\frac{z_z F(\phi_H - \phi_S)}{RT}\right] + k_b^1 \exp\left[-\frac{-z_o F(\phi_H - \phi_S)}{RT}\right] \right\}^{\frac{1}{2}}} \quad (\text{III-2})$$

where Z_z and Z_o are the valences of ions Z and O with their sign, respectively. When $K \ll 1$, the term in k_f can be neglected.

A similar equation can be written for a pseudo first order process



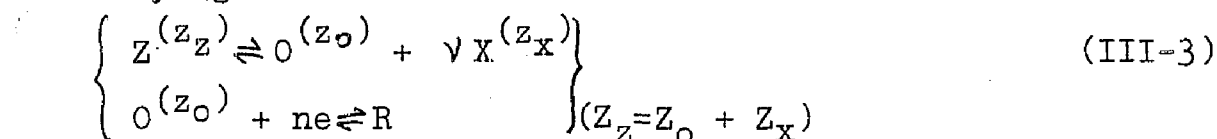
when Y is present in large excess and is not reduced or oxidized. The foregoing correction can also be applied to the plot of $I_d t^{\frac{1}{2}}$ versus I_d (I_d , diffusion currents) used by Ruetschi (19) for the study of kinetic currents in polarography.

The correction for the double layer structure depends on the valence of the species that are involved. Thus the corrective terms cancel out for the pseudo first order dissociation of a weak acid in presence of a large excess of anion.

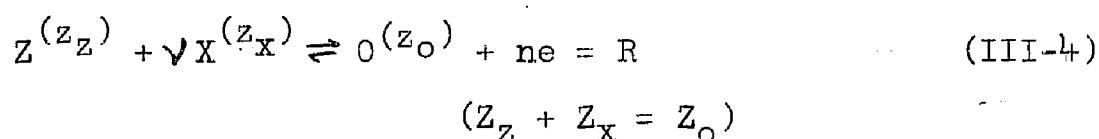
Detailed Treatment.

A more rigorous analysis in which the double layer structure is considered in the solution of the boundary value problem was recently developed by Gierst and Hurwitz (20). In

this laboratory, Matsuda (21) considered the same problem for conditions somewhat more general than those considered by the former authors. Equations were derived for the limiting current in polarography and the transition time in chronopotentiometry (galvanostatic method) for the reactions



and



where Z and X are not reduced or oxidized at the potential at which substance O is reduced.

Matsuda developed his treatment by introducing the following assumptions:

(i) The solution contains a large excess of indifferent z-z electrolyte, which essentially determines the double layer structure.

(ii) The thicknesses of the diffuse double layer $\frac{1}{K}$ and the reaction layer μ are very small in comparison with the diffusion layer thickness δ , and consequently the time-variation of the concentrations of substances O and Z within the former two layers can be neglected.

(iii) The solution contains a large excess of substance X in comparison with the concentrations of O and Z. The concentration distribution of X thus is independent of time during electrolysis and is not influenced by current flowing.

(iv) The equilibrium between substances O and Y is greatly in favor of Y.

Since the flux of Y at the Helmholtz plane is zero and the thicknesses $\frac{1}{k}$ and μ are very small, it can be assumed that the concentration of Z in the diffuse double layer and reaction layer is much larger than that of O. Hence, the concentration distribution of Z in these two layers is given by the Boltzmann distribution of equation II-2.

Matsuda's treatment is rather involved and the interested reader is referred to the original paper for details. His procedure can be briefly summarized as follows for reaction III-3 (basically the same approach is followed for reaction III-4):

The concentration distribution of O is a solution of equation

$$D_o \frac{\partial}{\partial x} \left\{ \frac{\partial C_o}{\partial x} + \left(\frac{z_o F}{RT} \right) C_o \frac{\partial (\phi_H - \phi_S)}{\partial x} \right\} + \left\{ k_f C_z^s \exp \left[\frac{z_z F (\phi_H - \phi_S)}{RT} \right] - k_b (C_x^o)^{\gamma} \exp \left[\frac{-\gamma z_x F (\phi_H - \phi_S)}{RT} \right] C_o \right\} = 0 \quad (\text{III-5})$$

with the boundary condition

$$\left(\frac{I}{nF} \right) = D_o \left\{ \frac{\partial C_o}{\partial x} + \left(\frac{z_o F}{RT} \right) C_o \frac{\partial (\phi_H - \phi_S)}{\partial x} \right\}_{x=0} \quad (\text{III-6})$$

The solution of equation III-5 is

$$C_o^* = \exp \left[\frac{-z_o (\phi_H - \phi_S)}{RT} \right] K_d (C_x^o)^{-\gamma} \left\{ C_z^s - \frac{(I / n F D_o^{\frac{1}{2}}) G_I}{K_d [k_b / (C_x^o)^{\gamma}]^{\frac{1}{2}}} \right\} \quad (\text{III-7})$$

where K_d is the dissociation constant of the complex and G_I is a function depending on the characteristics of the double layer structure. The expression for G_I , which is quite in-

volved is given by Matsuda (see Fig. 3) for different values of $\frac{l}{\kappa\mu}$, where $\frac{l}{\kappa}$ is the thickness of the diffuse double layer, which is a function of the charge and concentration of the supporting electrolyte.

Equation III-7 is identical with the result derived without consideration of the double layer structure except for the function G_I . Correction of previous treatments in polarography and chronopotentiometry is thus immediate. In particular, in the case of a polarographic kinetic current corresponding to the reaction $A \rightleftharpoons O + ne = R$ one has according to Matsuda

$$\log \frac{i_d - i}{i} + 1/2 \log t = \log G_I + \text{constant} \quad (\text{III-8})$$

where i_d is the diffusion current which would be observed in absence of a double layer effect, i the observed current, and t the drop time. By application of equation III-8 at two different values of $(\phi_H - \phi_S)$ and subtraction of one value from the other, one obtains the corresponding difference in $\log G_I$. An approximate value of $\frac{l}{\kappa}$ is then deduced by comparison of the calculated difference between the $\log G_I$ with the values given by Matsuda. Since $\frac{l}{\kappa}$ is known, the quantity μ is readily obtained. Since $\mu = \left(\frac{D_O}{k_b (C_X^O)} \right)^{\frac{1}{2}}$ k_b is obtained, and k_f can be computed if K_d is known. Also since μ has thus been determined, G_I , and hence C_O^* , can be calculated.

Matsuda's treatment predicts a peak in the current-potential polarographic curves - an effect which is actually observed for the discharge of cadmium from a cyanide solution (see Chapter VII). The treatment of Gierst and Hurwitz (20)

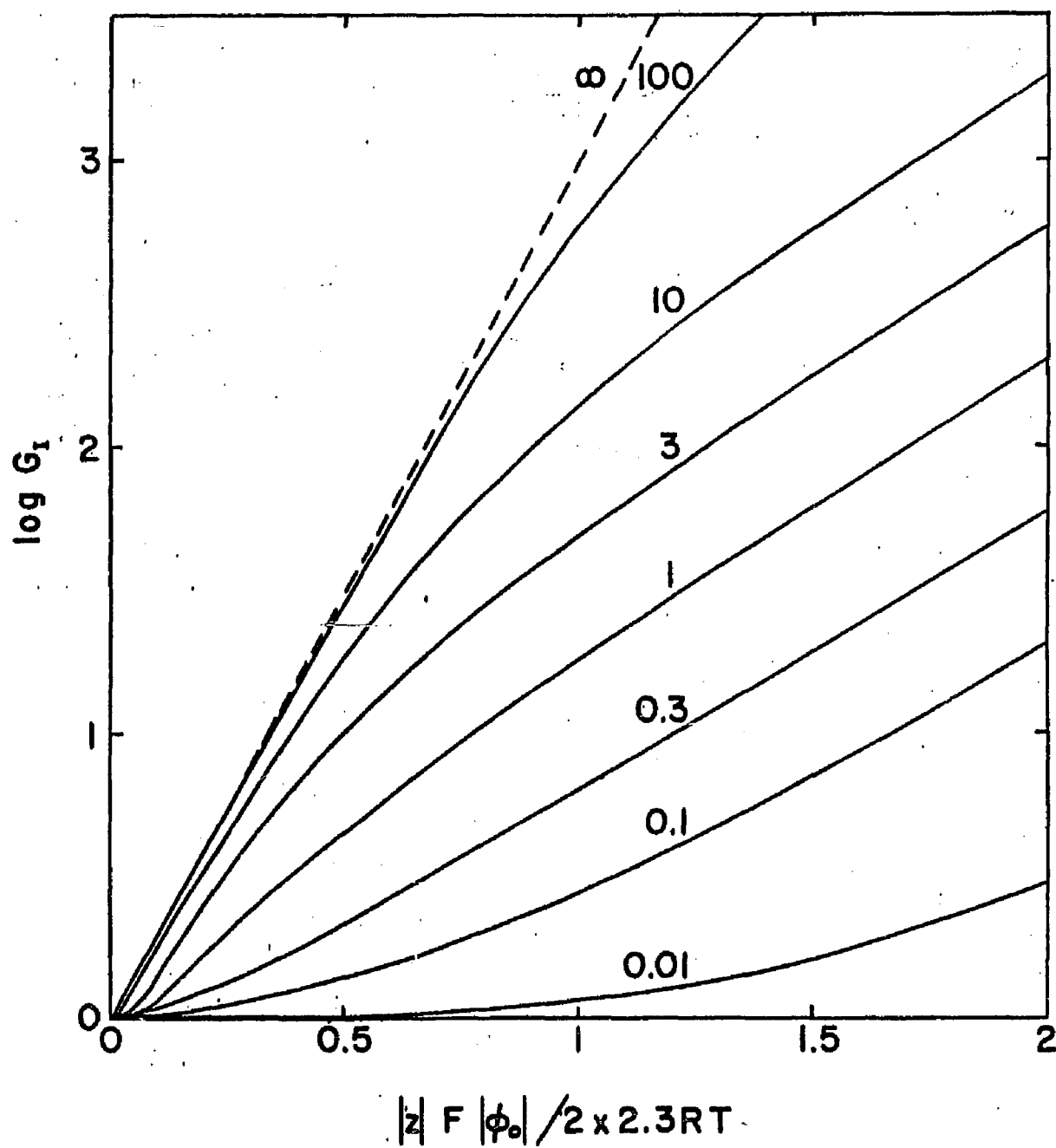


Fig. 3.- Variation of $\log G_1$ with $|z| F |\phi_o| / 2 \times 2.3 RT$ for different values of

also predicts a similar peak.

CHAPTER IV

EXPERIMENTAL

Solutions.

Solutions used in this work were prepared from Analytical Grade reagents. Further treatment was as follows: sodium cyanide, which was purified by passing a stock solution of the salt over charcoal that had been purified by treatment with hydrochloric acid in Soxhlet apparatus for two weeks (22) and sodium sulfate and sodium chloride were heated for several hours at about 500 degrees C to destroy organic matter.

Amalgams.

A stock thallium amalgam was prepared by electrolysis of a saturated solution of thallous sulfate at a stirred mercury electrode. A platinum foil was used as anode. Qualitative tests on the salt indicated negligible concentrations of heavy metals other than thallium. The solution was kept saturated by repeated addition of solid thallous sulfate. No critical conditions were required for electrodeposition. The concentrated amalgam was kept at a potential of -0.7 V (vs.S.C.E.) for several hours in a solution of 5% sulfuric acid, which was renewed at short intervals (about fifteen minutes). This was done to eliminate traces of metals less noble than thallium. Some thallium was lost in this operation, but this was not im-

portant since in all cases the amalgams were analyzed before use.

Three thallium amalgams of the following concentrations were prepared: $3.45 \pm 0.05\%$; $10.0 \pm 0.1\%$ and 31% .

An all-glass apparatus was used for the dropping thallium amalgam electrodes, except for a very short piece of rubber tubing used to join the amalgam reservoir to a piece of soft glass tubing terminated by the polarographic capillary. It was observed that Tygon tubing develops a brownish color in contact with the amalgam, and for this reason its use was avoided. The bottom of the amalgam reservoir was fitted with a ground glass plunger which allowed one to interrupt the flow of amalgam at will. This plunger, when properly ground, was quite leak-free.

The following procedure was used to fill the electrode assembly: the reservoir was evacuated and pure mercury was sucked into the capillary up to a very small section of the connecting glass tube. Then the amalgam was quickly vacuum-pumped into the reservoir from the top.

The oxidation of the amalgam in the reservoir by air was prevented by making the amalgam the cathode of an electrolytic cell, the anode being a piece of platinum foil. One-tenth molar sulfuric acid was added on top of the amalgam, which was negatively polarized so that slow evolution of hydrogen could be detected.

A polarographic H-cell was used as electrolysis vessel, the solution under study being in both arms of the cell. The amalgam electrode entered one arm while the other arm was connected to a saturated calomel electrode through a salt bridge. Thus contamination of the solution in the electrolysis compartment by potassium chloride was avoided. For A.C. impedance measurements a third electrode, i.e. a platinum cylinder of about 1.5 cm diameter, and coaxial with the capillary of the dropping amalgam, was inserted in the cell.

The amalgam flowing from the capillary was analyzed as follows: samples whose weight depended on the approximate thallium concentration were dissolved in 1:1 nitric acid and the solutions slowly evaporated until dryness. The residue was digested hot with at least five successive portions of 10-15 ml. of water. Sodium sulfate and water were then added to make 250 ml. 0.1 M in sodium sulfate. After the precipitate settled, 50 ml. of the solution were diluted to a final volume of 100 or 250 ml. with 0.1 M sodium sulfate. The final solution which also contained 0.0002% Triton X-100 as maximum suppressor, was analyzed polarographically. A solution containing a known amount of thallous nitrate in 0.1 M sodium sulfate was used as a comparison standard. It was ascertained that no thallium was lost by analysis of mixtures of mercury with known amounts of thallium nitrate.

Determination of the point of zero charge of amalgams.

The point of zero charge E_z of the thallium amalgams

was determined from drop time measurements in 0.1 M sodium sulfate. The position of the electrocapillary maximum could not be readily determined because the plateaus of the curves were quite flat over a rather wide range of potentials. However, the shift of the negative "tail" of electrocapillary curves with respect to the curve for pure mercury could easily be determined. Since E_z is well known for mercury, the point of zero charge could be deduced from the shift of the electrocapillary curves. This procedure, however, is somewhat open to question.

Recording of Current Potential Curves.

A Sargent Polarograph Model XXI was used, the pen and ink recorder of which had been replaced by a faster recorder (1.2 seconds full-scale deflection). Currents were measured at the end of drop life for a cell temperature of 30.0 ± 0.2 degrees C.

A.C. Impedance Measurements.

Both faradaic and non-faradaic parameters were measured with an A.C. impedance bridge. The applied A.C. peak voltage never exceeded five millivolts. The bridge was balanced at the end of drop life.

Experimental Determination of the Exchange Current and Transfer Coefficient for the Hexacyanochromate II III Couple.

A 5×10^{-3} M solution of "Electronic Grade" potassium hexacyanochromate (III) from City Chemical Corporation, N.Y.C., was

prepared in 0.2M sodium cyanide. Since the reduced form is very unstable it was prepared in situ by the following method:

A polarogram was taken of the $5 \times 10^{-3}M$ solution of potassium hexacyanochromate (III) and the half-wave potential was carefully measured. Then the dropping (mercury or amalgam) electrode was kept at the half-wave potential while the polarization resistance of the couple was measured at several frequencies. Both the oxidized and the reduced forms of the couple had the same concentration of $2.5 \times 10^{-3}M$ at the electrode surface. The exchange current density I_0 was calculated from the polarization resistance extrapolated at infinite frequency by the equation

$$R_p = \frac{RT}{nFA} \frac{1}{I_0} \quad (IV-1)$$

where A is the electrode area.

The transfer coefficient was determined from the variations of I_0 with the ratio of hexacyanochromate (III) to hexacyanochromate (II) at the electrode surface. Thus one deduces by dividing both sides of equation (II-9) by C_O^0 and taking the logarithm that at constant $\phi_H - \phi_S$

$$\log \frac{I_0}{C_O^0} = \text{constant} + \log \frac{C_O^0}{C_R^0} \quad (IV-2)$$

The ratio C_O^0/C_R^0 in the case of hexacyanochromate varied by change of the potential at which the faradaic impedance was measured, and the concentration ratio was calculated from classical polarographic theory.

CHAPTER V

EXPERIMENTAL RESULTS

INFLUENCE OF ELECTROLYTE CONCENTRATION

REDUCTION OF IODATE ION ON A DROPPING HG ELECTRODE

Iodate ion is reduced in alkaline solution ($\text{pH} > 12$) on mercury at potentials (for a given current density) which are independent of pH. At 10^{-5} - 10^{-4} amp. cm.^{-2} potentials are in the range -1.0 to -1.2 volts (vs. S.C.E.), ie. outside the range of specific adsorption of the anions I^- , IO_3^- , OH^- . The effect of electrolytes on the reduction of iodate was previously studied in this laboratory under polarographic conditions by application of the treatment of irreversible waves (23). Results were explained on the assumption that cations reduce the electrostatic repulsion of iodate ions by the electrode.

Linear plots of E versus $\log I$ (I , instantaneous current at the end of drop life) were obtained (Fig. 4) with a dropping mercury electrode in the absence of practically any concentration polarization ($I < 0.01 I_d$). Plots of $\log I$ versus E were shifted toward less negative potentials upon the addition of potassium chloride. The product, $\alpha n_a = 0.81$, was independent of electrolyte concentration and in good agreement with the value, $\alpha n_a = 0.77 \pm 0.02$ previously obtained by polarography. Similar results were obtained with lithium

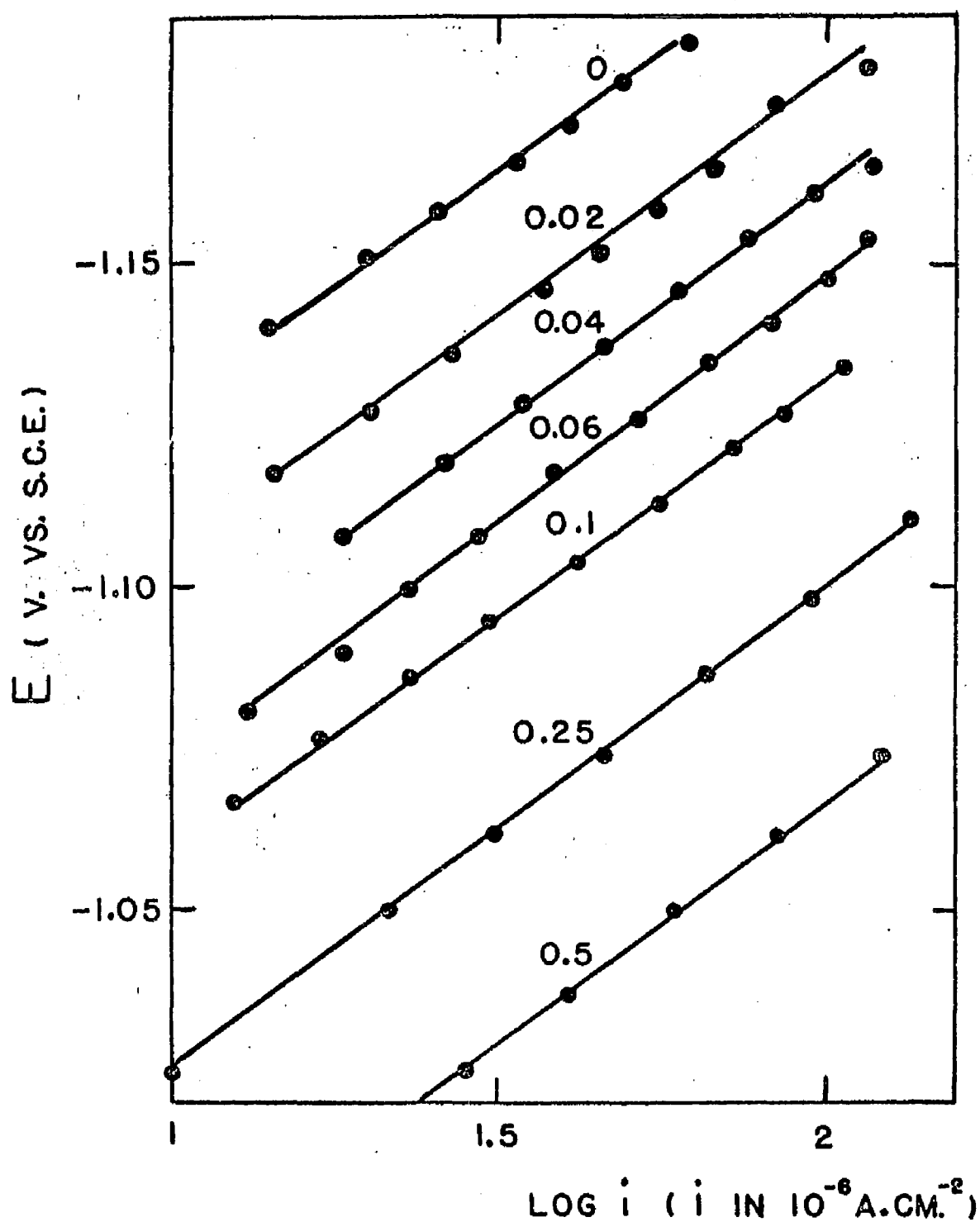


Fig. 4.- E versus $\log i$ for the reduction of $5 \times 10^{-3} \text{ M KIO}_3$ in $2 \times 10^{-2} \text{ M KOH}$ with varying molar concentrations of KCl at 30°C .

chloride and potassium sulfate.

Experimental and calculated shifts are compared in Table I. The agreement is good for potassium and lithium chloride but not entirely satisfactory for potassium sulfate. Anyhow, it is concluded that changes in the double layer structure upon the addition of electrolyte essentially account for the salt effect in the reduction of iodate on mercury in alkaline media.

Approximate values of the shift ΔE calculated from equation (II-7) are also listed in Table I to indicate the approximation achieved by this equation, especially for large changes in electrolyte concentration. It was assumed in this calculation that the constant of equation (II-7) is independent of potential over the interval ΔE .

Data used in these computations and not previously quoted were as follows: Point of zero charge: $E_z = -0.45$ volt versus S.C.E.; $T = 303.1$; $\epsilon = 79$. The integral capacity K_1 hardly varied between -1.0 and -1.2 volts (vs. S.C.E.), and consequently the K_1 's at -1.1 volts (vs. S.C.E.) were used. The following values in units, microfarads. cm^{-2} , were determined and additional ones were interpolated. For KCl series: 16.4 (no KCl added), 16.7 (0.02M KCl), 19.6 (0.5M KCl). For Li Cl: 16.0 (no LiCl added), 16.6 (0.02 M), 20.4 (0.5 M). For $K_2 SO_4$: 16.5 (no $K_2 SO_4$ added), 17 (0.02M), 18.8 (0.5M).

Liquid junction potentials were quite negligible. For

TABLE I

Comparison of Experimental and Calculated Shifts ΔE for
Reduction of 5×10^{-3} M Iodate in 2×10^{-2} M Hydroxide With
Varying Amount of Electrolyte at 30°C .

$C_{\text{salt}},$ mole l.	$E_{\text{exp.}}$ v. vs. S.C.E.	$E_{\text{exp.}}$ v.	$E_{\text{calcd.,}}$ rigorous, v.	$E_{\text{calcd.,}}$ approximate (eq.7) v.
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$\text{KIO}_3 + \text{KOH} + \text{KCl}^{\text{a}}$

0.00	-1.173
.02	-1.149	0.022	0.030	0.034
.04	-1.135	0.039	0.047	0.055
.06	-1.119	.054	.060	.071
.10	-1.104	.069	.078	.094
.25	-1.073	.102	.111	.140
.50	-1.039	.136	.133	.177

$\text{LiIO}_3 + \text{LiOH} + \text{LiCl}^{\text{b}}$

0.00	-1.151
.02	-1.125	0.026	0.025	0.034
.04	-1.109	.042	.042	.055
.06	-1.097	.054	.054	.071
.10	-1.079	.072	.071	.094
.25	-1.037	.114	.103	.140
.50	-1.004	.147	.127	.177

$\text{KIO}_3 + \text{KOH} + \text{K}_2\text{SO}_4^{\text{c}}$

0.00	-1.157
.02	-1.127	0.030	0.047	0.056
.04	-1.101	.056	.072	.084
.06	-1.087	.070	.087	.103
.10	-1.070	.087	.102	.122
.25	-1.042	.115	.142	.175
.50	-1.018	.139	.169	.214

^aAt 40 microamp. cm. ⁻². ^bAt 27 microamp. cm. ⁻².

^cSame as b.

KCl series: -2.5 mV. without addition of KCl; -1.1 mV. for the 0.5 M KCl solution. For the K_2SO_4 series: + 3.9 mV. for the 0.5 M solution. No evaluation was made for LiCl. The minus sign indicates that the liquid junction potential was positive from the reference electrode to the dropping mercury electrode.

CHAPTER VI
EXPERIMENTAL RESULTS
INFLUENCE OF THE NATURE OF THE ELECTRODE

As was pointed out in the Introduction (Chapter I), thallium amalgams of different thallium concentrations were used to study the effect of the nature of the electrode on electrochemical kinetics. This electrode was chosen because the point of zero charge E_z of the electrode, in absence of specific adsorption, can be changed continuously from -0.45 to about -0.9 volts (versus S.C.E) simply by variation of the thallium concentration. Besides, amalgams are easy to prepare and handle, and they can be used in the same manner as dropping mercury electrodes.

The zero points of thallium amalgams of different thallium concentrations had been studied first by Frumkin and Gorodetskaya (24). Using a solution of 1M sodium sulfate and a Lippmann capillary electrometer, these authors determined for several concentrations of thallium the E_z values shown in Table II. The writer used the drop time method (see Chapter IV) and obtained the values also listed in Table II.

The two sets of data differ somewhat but it is not known which one is more reliable. On one hand the drop time method is less accurate than Lippmann's method, assuming no contamination of the electrode from impurities in the solution occurs.

TABLE II

Points of Zero Charge E_z as a Function of
Thallium Concentration in Thallium Amalgams

% Tl	E_z (Volts vs S.C.E.)
Frumkin and Gorodetskaya	
3.35	-0.69
10.35	-0.76
33.9	-0.88

This work

3.45	-0.57
10.0	-0.68
31.	-0.85

On the other hand, a non-renewable electrode surface is in contact with the solution for a rather long time in the capillary electrometer, and contamination of the electrode is likely to occur unless extremely pure solutions are used. At the time the work of the Russian workers was published (1928) the role of small concentrations of impurities was in general not realized, and indeed Frumkin and Gorodetzkaya do not mention in their article any special purification procedure for their solutions. Both sets of E_2 values were used in this work. Since the amalgams had nearly the same thallium concentrations as those of Frumkin and Garodetzkaya their set of values could be used for comparison purposes.

Experimental Study of the Reduction of Bromate Ion.

The reduction of bromate had been studied among other investigators, by Orlemann and Kolthoff (25) and by Gierst (9). Only the latter considered double layer effects, and his work was restricted to the dropping mercury electrode. In this work the effect of the nature of the electrode is considered. This electrode reaction was chosen because (a) it is markedly irreversible, (b) its kinetics is pH-independent for $\text{pH} > 12$; (c) it occurs at polarographic current densities at potentials at which oxidation of thallium amalgam is negligible; (d) there is no specific adsorption of bromate ion because of the markedly negative potentials with respect to the points of zero charge for the amalgam electrodes, at which this reaction occurs.

TABLE III

Potential Difference Across Diffuse Double Layer and
Thallium Concentration in Amalgam at -1.6 Volts Versus S.C.E.

Thallium Concentration (In Percent)	$\phi_H - \phi_S$ (Volts)	
	Frumkin and Gorodetskaya	This Work
0.0	-0.113	-0.113
3.45	-0.105	-0.111
10.0	-0.104	-0.109
31.	-0.103	-0.105

TABLE IV

Values of $\Delta E / \Delta(\phi_H - \phi_S)$ With
Respect to the Dropping Mercury Electrode
in the Reduction of Bromate Ions

Electrode	Calculated	Observed	
		Frumkin's E_z	This Work
10.0% Tl	3	1.0	2.25
31. % Tl	3	4.3	5.25

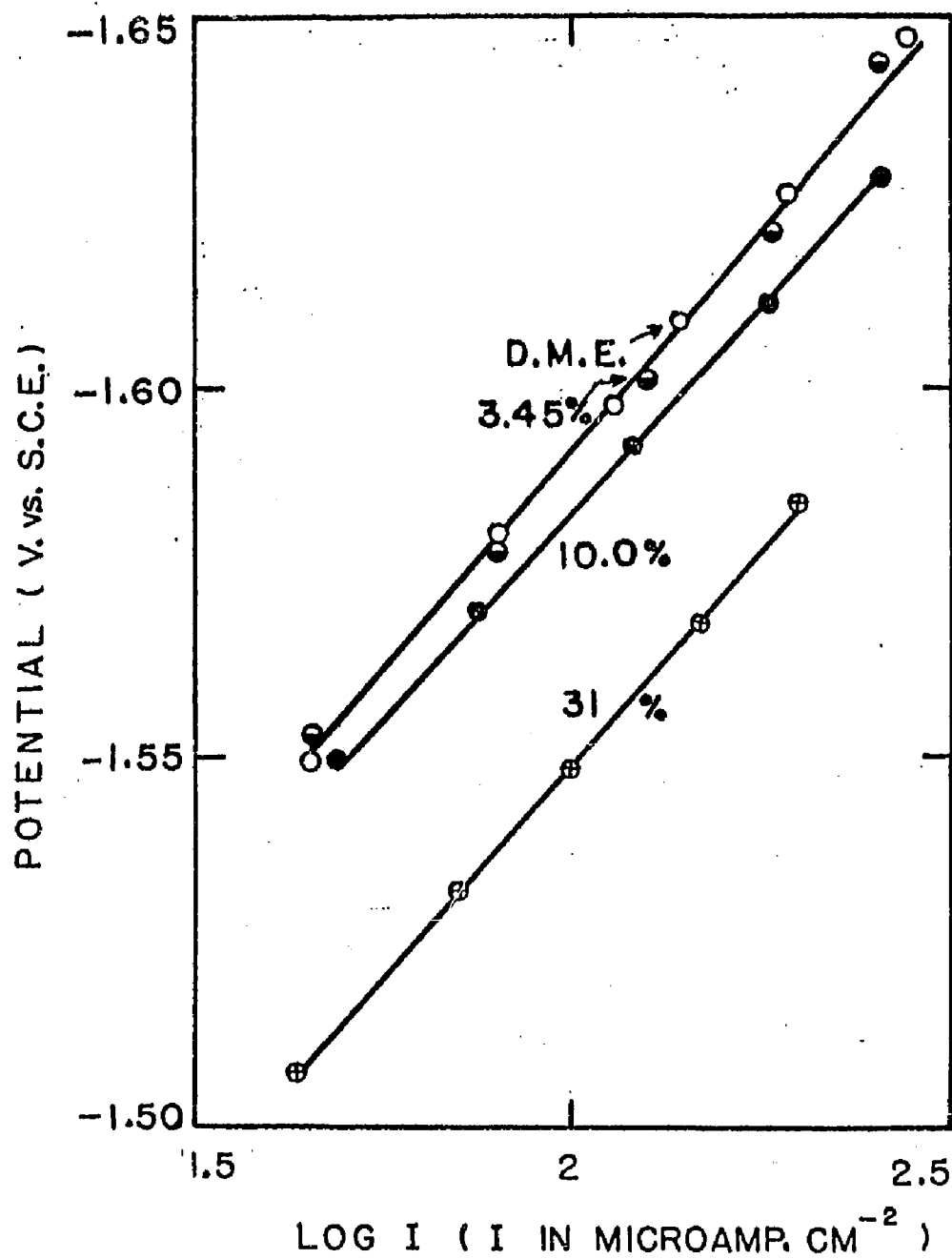


Fig. 5.- E versus $\log I$ for the reduction of 5×10^{-3} M NaBrO_3 in 0.1 M NaCl and 5×10^{-2} M NaOH at a dropping mercury and dropping Tl amalgam electrodes of different Tl concentration. Temperature: 30°C

Figure (5) shows linear plots of E versus $\log I$ for the four electrodes used. Note that there is practically no shift ΔE in the lines obtained with the dropping mercury electrode and the 3.45% thallium amalgam. The calculated values of $(\phi_H - \phi_S)$ at $E = -1.6$ volts (versus S.C.E.) for each of the electrodes are shown in Table III using the E_z values of Frumkin and Gorodetzkaya and those determined in this work.

Using equation II-3 and the value of $n_a = 0.5$ determined from the slope of the $\log I$ versus E plots, the theoretical value of the voltage shift ΔE corresponding to a change in $(\phi_H - \phi_S)$ was found to be $\Delta E = 3 \Delta(\phi_H - \phi_S)$. The experimentally determined values are shown in Table IV.

Using the curve for the dropping mercury electrode as reference one concludes that a better agreement for the 10% Tl amalgam was obtained with the values of E_z determined in this work than with the value determined by Frumkin and Gorodetzkaya. In the case of the more concentrated amalgam the values of E_z (Frumkin's and the author's) differ by only 2 millivolts. Yet this small difference in $(\phi_H - \phi_S)$ causes a difference in ΔE of about 20%.

Experimental Study of the Reduction of Chromate Ion.

Double layer effects in the reduction of chromate ions have been studied extensively by Gierst (9) with a dropping mercury electrode. The observed double layer effects were quite large. This was to be expected since the charge of the

chromate ion is $z=-2$. For this reason we chose this reaction in the study of the effect of the nature of the electrode on electrode reactions.

Polarograms for dropping thallium amalgams at different concentrations of sodium hydroxide are shown in Fig. (6). Note that the limiting current is attained at potentials much more positive than in the case of the dropping mercury electrode (about -1.3 volts versus S.C.E.) This shift is due to a double layer effect.

The pronounced minima in the current-potential curves are similar to the ones first studied by Kryukova (26)* and subsequently by Frumkin and co-workers (5) for several anions. It is generally accepted that the dip in the current-potential curve is caused by electrostatic repulsion of the anions by the negatively charged electrode. An expression for a quantitative relationship between the current and the value of $(\phi_H - \phi_S)$ can be derived as follows:

Equation II-1 is written with C^* expressed in terms of C_s (equation II-2). This gives

$$I = kC_s \exp \left\{ - \frac{\alpha n_a F}{RT} \left[E - \frac{\alpha n_a - z}{\alpha n_a} (\phi_H - \phi_S) \right] \right\} \quad (VI-1)$$

Equation (VI-1) does not take into account concentration

*In fact the first case was reported by Kolthoff and Matsuyama for the reduction of complex nickel thiocyanate (Ind. Eng. Chem., Anal. Ed. 17, 615, (1945), but they did not go beyond mentioning the fact.

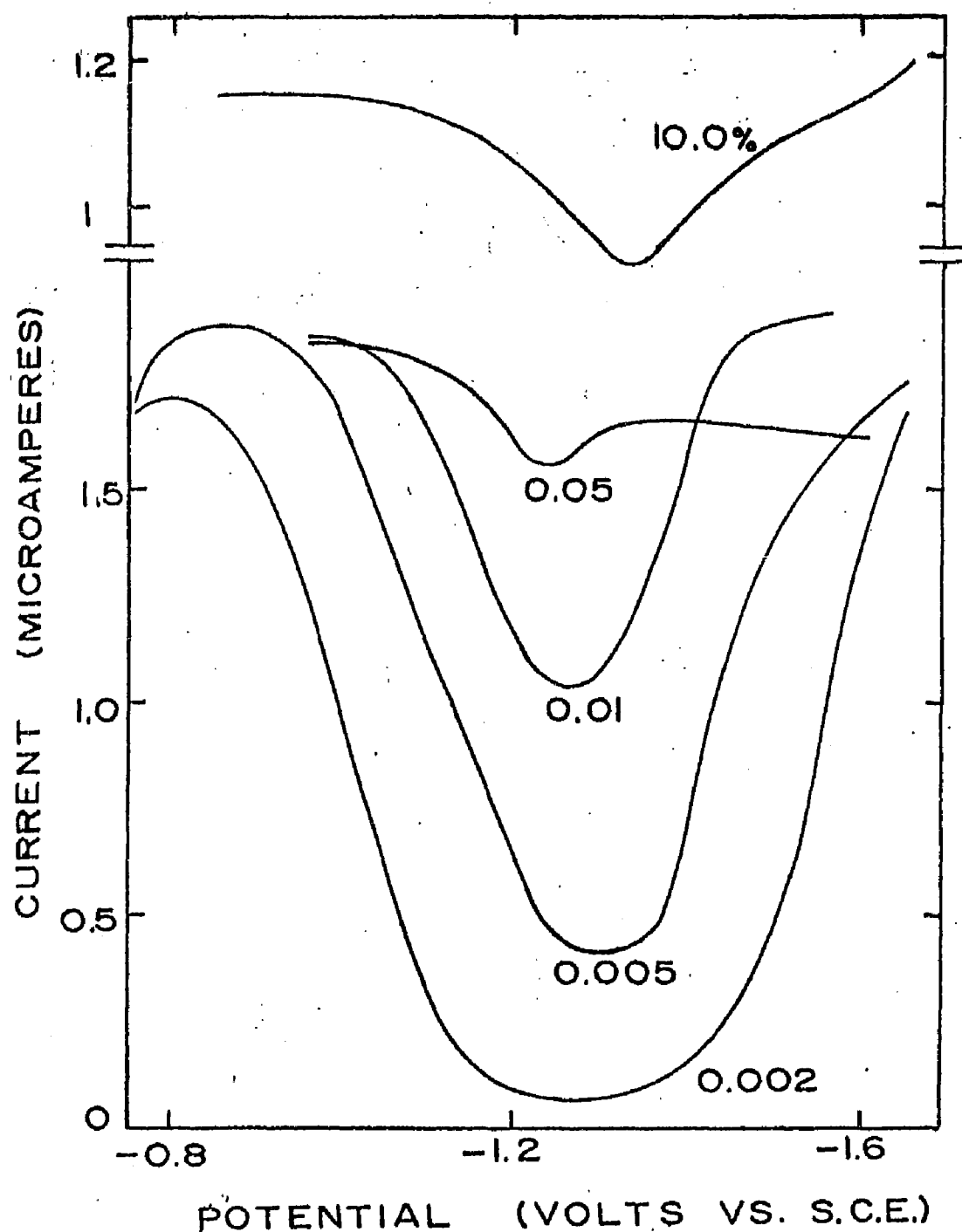


Fig. 6.- I versus E in the reduction of $10^{-4} \text{ M Na}_2\text{CrO}_4$. The four lower curves were obtained at the 3.45% Tl amalgam for different molar concentrations of NaOH. The upper curve was obtained for the 10% Tl amalgam with 10^{-2} M NaOH . Temperature: 30°C

polarization. If this is taken into consideration, we must multiply C_s by $(1 - \frac{I}{I_d})$, thus obtaining

$$I = kC_s \left(1 - \frac{I}{I_d} \right) \exp \left\{ - \frac{\alpha n_a F}{RT} \left[E - \frac{\alpha n_a - z}{\alpha n_a} (\phi_H - \phi_S) \right] \right\} \quad (\text{VI-2})$$

or since I_d is constant for given conditions of electrolysis

$$\log \frac{I}{I_d - I} = \text{constant} + \frac{\alpha n_a F}{2.3RT} \left[-E + \frac{\alpha n_a - z}{\alpha n_a} (\phi_H - \phi_S) \right] \quad (\text{VI-3})$$

At constant E we get

$$\log \frac{I}{I_d - I} = \text{constant} + \frac{F}{2.3RT} (\alpha n_a - z) (\phi_H - \phi_S) \quad (\text{VI-4})$$

Equation (VI-4) shows that a plot of $\log (I/I_d - I)$ against $\phi_H - \phi_S$ at a constant potential E is linear with a slope of

$$\frac{F}{2.3RT} (\alpha n_a - z)$$

An alternative approach uses Koutecky's treatment of irreversible polarographic waves (27). From the measured values of I/I_d we determine the parameter $\lambda = \frac{k_f t^{\frac{1}{2}}}{D^{\frac{1}{2}}}$, in which t is the drop time and D the diffusion coefficient of the substance being reduced (or oxidized) at the electrode. Since we can measure t , and $D^{\frac{1}{2}}$ can be easily calculated from the diffusion current of the reduction of chromate and the capillary characteristics, we find k_f , the apparent rate constant of the cathodic reaction. Now $I = nF k_f C^*$. i.e. I is proportional to $k_f C^*$,

$$I = kC^* \exp \left[- \frac{\alpha n_a F E}{RT} \right] \exp \left[\frac{(\alpha n_a - z) F (\phi_H - \phi_S)}{RT} \right] \quad (\text{VI-5})$$

and consequently at constant potential, I is proportional to

$$C^* \exp \left[\frac{(\alpha n_a - z)}{RT} F (\phi_H - \phi_S) \right]$$

Hence I/C^* and consequently k_f (see Equation VI-2) is proportional to

$$\exp \left[\frac{(\alpha n_a - z) F (\phi_H - \phi_S)}{RT} \right], \text{ i. e.}$$

$$\log k_f = P + \frac{(\alpha n_a - z) F}{2.3RT} (\phi_H - \phi_S) \quad (\text{VI-6})$$

where P is a constant. Equation (VI-7) shows that a plot of $\log k_f$ against $(\phi_H - \phi_S)$ at a constant potential E is linear with a slope $\frac{F}{2.3RT} (\alpha n_a - z)$.

Both equations (VI-1) and (VI-4) were applied to analyze the curves obtained with the 3.45% thallium amalgam at $E = -1.10$ volt (versus S.C.E.) The corresponding plots are shown in Fig. (7) for the values of $\phi_H - \phi_S$ obtained by Frumkin and Gorodetz-kaya. The slopes obtained are in reasonable agreement if we consider that we have only 3 points for each plot. The values of $z - \alpha n_a$ are -2.43 ± 0.13 , with $z = -2$. The value of αn_a cannot be accurately determined from the slopes of these plots since αn_a is much smaller than the absolute value of $z(-2)$. An independent determination of αn_a is therefore desirable. This can easily be carried out from the current-potential curve obtained with the dropping mercury electrode and the well known equation

$$\log k_f = \text{constant} - \frac{\alpha n_a F E}{2.3RT} \quad (\text{VI-7})$$

Equation (VI-7) was applied to the polarograms obtained with two solutions containing $2 \times 10^{-4} \text{ M Na}_2\text{CrO}_4$, one of them containing 0.01 M NaOH and the other 0.002 M NaOH . The value of αn_a obtained was 0.42 ± 0.02 , in good agreement with the value of 0.43 ± 0.13 obtained with the thallium amalgams at

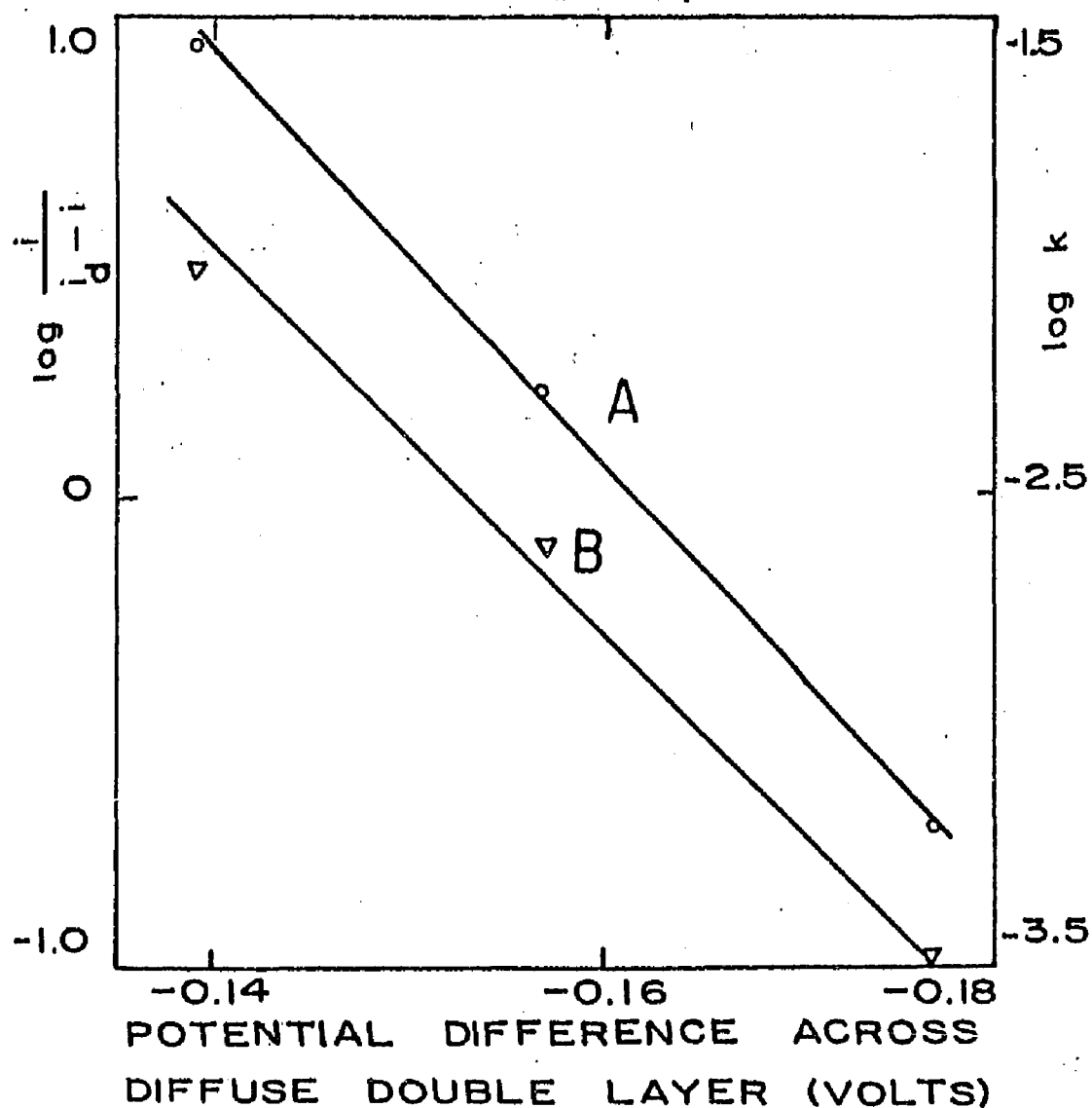


Fig. 7.- $\log 1/(i_d - i)$ versus $\phi_H - \phi_s$ (A) and $\log k$ versus $\phi_H - \phi_s$ (B) for the reduction of $10^{-4}M$ Na_2CrO_4 at a 3.45% Tl amalgam with $10^{-2}M$, $5 \times 10^{-3}M$ and $2 \times 10^{-3}M$ $NaOH$. Each value of $\phi_H - \phi_s$ corresponds to a different $NaOH$ concentration. Temperature: $30^\circ C$

constant E.

Exchange Current for the Couple $\text{Cr}(\text{CN})_6^{-3} + e \rightleftharpoons \text{Cr}(\text{CN})_6^{-4}$.

In Chapter II the expression II-9 for the exchange current for a reversible electrode process was developed. Application is made here to the exchange current between the hexacyanochromate (III) and the hexacyanochromate (II) anions. This system was chosen because the redox partners have a high charge, and the reaction occurs at a very negative potential (-1.4 volts versus S.C.E.) with respect to the points of zero charge of the electrodes used. A very pronounced double layer effect would be expected. In fact, a large double layer effect had already been observed by Randles and Somerton (28) at a dropping mercury electrode using different concentrations of inert electrolyte. The results obtained in this work with the four different electrodes, however, show only a very small effect (see Table V). This was puzzling at first, but the results can easily be explained after examining the C_d -E plots shown in Fig. 8. From equations (II-5) and (II-6) it is known that an increase in both $(E-E_Z)$ and K_i increase the value of $(\phi_H - \phi_S)$, other quantities being equal. In this particular case the effect of the decrease in $(E-E_Z)$ from pure mercury to the thallium amalgams is offset by the increase in the value of K_i and consequently the $(\phi_H - \phi_S)$ values for the four electrodes are not very different.

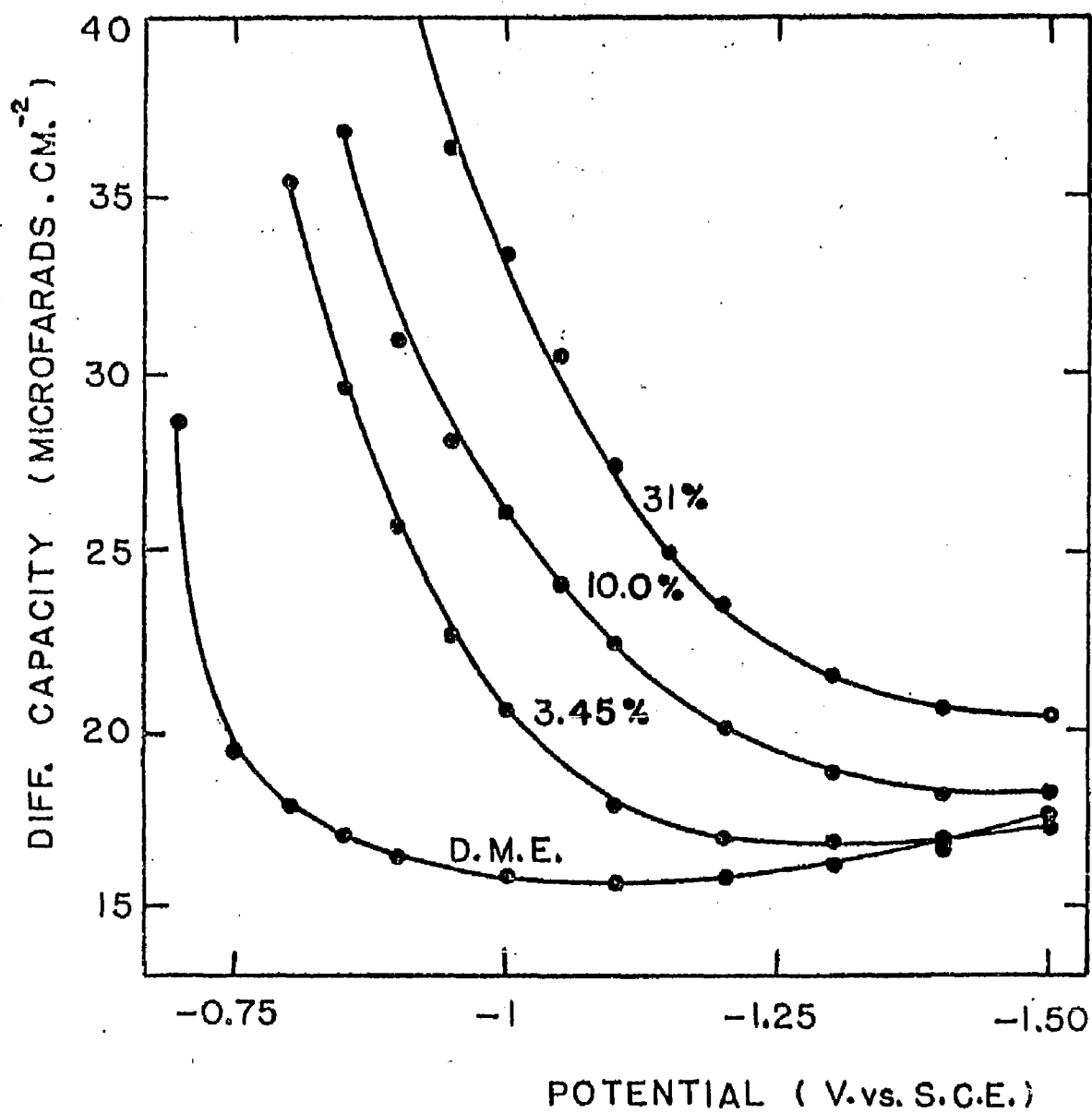


Fig. 8.- C_d versus E for the dropping Hg and Tl amalgam electrodes in 0.2 M NaCN, at 30°C.

TABLE V

Results on Reaction $\text{Cr}(\text{CN})_6^{-3} + e \rightleftharpoons \text{Cr}(\text{CN})_6^{-4}$

	<u>DME</u>	<u>3.45% Tl</u>	<u>10.0% Tl</u>	<u>31% Tl</u>
$I_0 \times 10^3 \text{ amp/cm}^2$	3.9	3.9	3.9	4.8
$(\phi_H - \phi_S)$ (Frumkin, volts vs S.C.E.)	0.675	0.73
$(\phi_H - \phi_S)$ (This Work, volts vs S.C.E.)	-0.0905	-0.086	-0.085	-0.077
$(\phi_H - \phi_S)$ (This Work, volts vs S.C.E.)	-0.0905	-0.097	-0.0945	-0.084

CHAPTER VII
EXPERIMENTAL RESULTS
DISCHARGE OF CADMIUM CYANIDE
WITH PRECEDING CHEMICAL REACTION

The discharge of cadmium metal from a cyanide solution has been extensively studied by several investigators (29-32). In presence of a large excess of cyanide, the cadmium in solution is present as $\text{Cd}(\text{CN})_4^-$. It has been established by Gerischer (30), Gierst (32) and Koryta (31) that the discharge proceeds via dissociation to $\text{Cd}(\text{CN})_3^-$. Besides, considerations of double layer effects were introduced independently by Gierst (32) and by Delahay and coworkers (10) (see Chapter III). In a very recent work (9) Gierst showed a very large double layer effect on a dropping mercury electrode using different concentrations of supporting electrolyte. In this work a considerable effect was observed for a given solution (10^{-3}M CdCl_2 , 0.1M NaCN) using the four different electrodes (Fig. 9.). Note that not only does the peak current vary from electrode to electrode (allowance being made for the difference in capillary characteristics), but that also the morphology of the curves is modified. This suggests that the dissociation to $\text{Cd}(\text{CN})_3^-$ is not the only rate-determining step, - at least for the 10% and 31% thallium amalgam electrodes -, but that there is a competing mechanism, and that the nature of the electrode determines the relative extent to which the

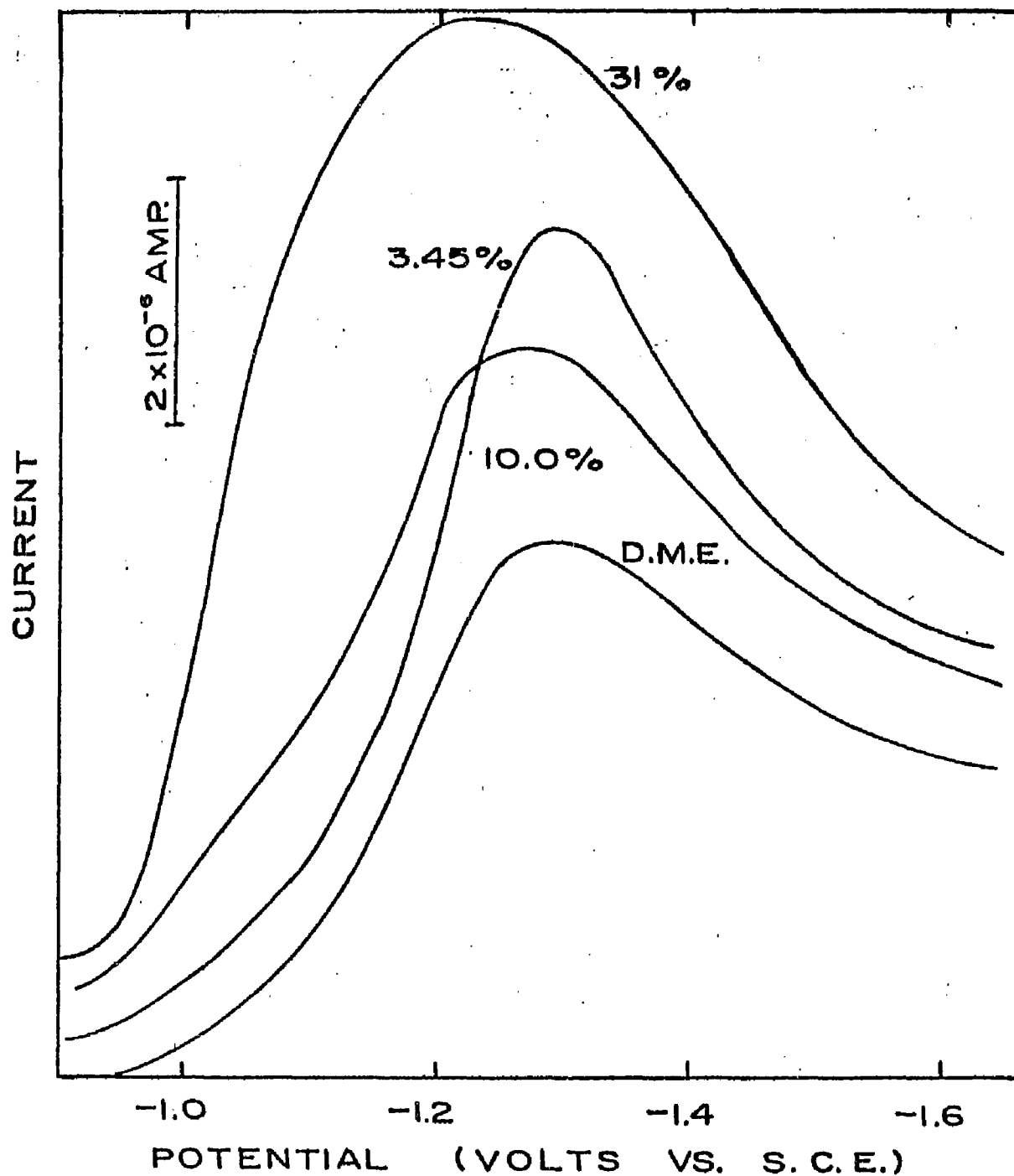


Fig. 9.- i versus E in the reduction of $10^{-3} \text{M Cd(CN)}_4^{2-}$ at the dropping mercury and Tl amalgam electrodes. values were:
 DME = 1.50; 3.45% Tl = 2.18; 10.0% Tl = 1.57; 31% Tl = 1.60. Supporting electrolyte: 0.1M NaCN. Temperature: 30°C

different reactions contribute to the total current. The peaks in the current-potential curves can be explained qualitatively by noting that the magnitude of $-(\phi_H - \phi_S)$ increases with increasing negative potential; hence the current decreases because of electrostatic repulsion of the reacting ions from the electrode surface. It has already been mentioned (see Chapter III) that a quantitative analysis of the current-potential curves was developed by Gierst and Hurwitz (20) and Matsuda (21). In this work Matsuda's treatment was applied to the curve obtained with the dropping mercury electrode. The values of $\log \frac{i_d - i}{i} + \frac{1}{2} \log t$ obtained at different points along the curve were plotted against $\frac{zF(\phi_H - \phi_S)}{2 \times 2.3RT}$ (i is the maximum current at the end of drop life). Since i_d cannot be directly determined for the complex it was assumed equal to the diffusion current obtained for the same concentration of CdCl_2 in 0.1M NaCl. It was realized that this could lead to some error. In order to estimate roughly the effect of an error in i_d on the validity of Matsuda's treatment two other values of i_d were arbitrarily chosen; one 10% above and the other 10% below that obtained for Cd Cl_2 in 0.1 M Na Cl, and the same analysis was used with the different chosen values of i_d . In all three cases a plot of $\log \frac{i}{i_d - i} + \frac{1}{2} \log t$ versus $\frac{zF(\phi_H - \phi_S)}{2 \times 2.3RT}$ corresponds to a value of $1/k\mu \approx 100$. (Fig. 10) Since $1/k \approx 10^{-7}$ cm. this gives $\mu \approx 10^{-9}$, which is too low by more than one order of magnitude. Therefore Matsuda's treatment is not valid in this case, the probable reason being that even for the dropping mercury electrode there may be more than one

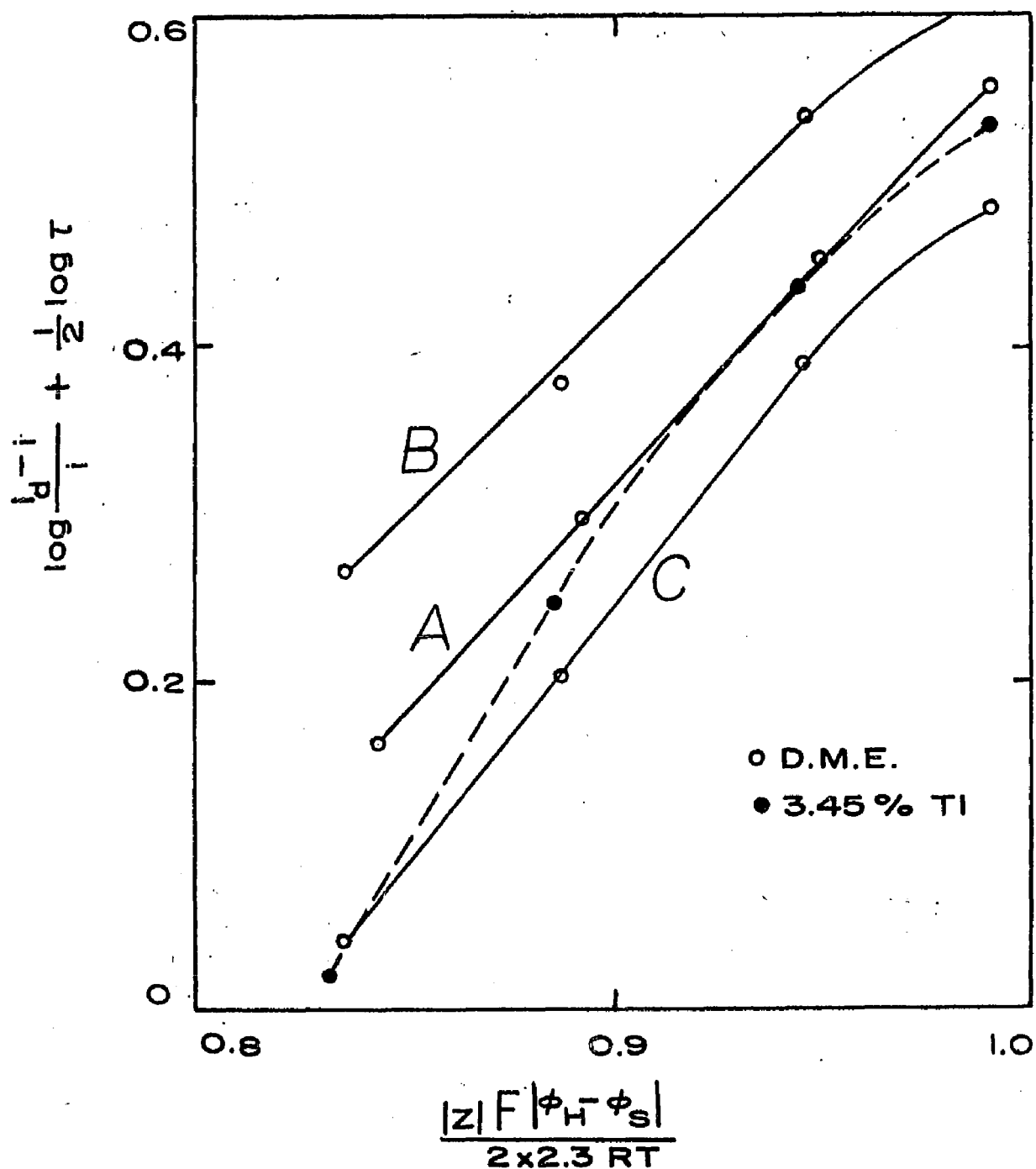


Fig. 10.- $\log (I_d - I)/I + \frac{1}{2} \log \tau$ versus $\frac{|z| F |\phi_H - \phi_S|}{2 \times 2.3 RT}$ for the reduction of $\text{Cd}(\text{CN})_4^{2-}$ in 0.1M NaCN. I_d values for curves B and C were arbitrarily chosen (B) 10% above and (C) 10% below that obtained for 10^{-3}M CdCl_2 in 0.1M NaCl and used in curve A.

mechanism for the over-all reaction, whereas Matsuda's treatment assumes only one mechanism.

A plot of $(\phi_H - \phi_S)$ vs E for the four electrodes used is shown in Fig. 11. Frumkin's set of values for E_z were used. Little difference is found with E_z values determined from this work.

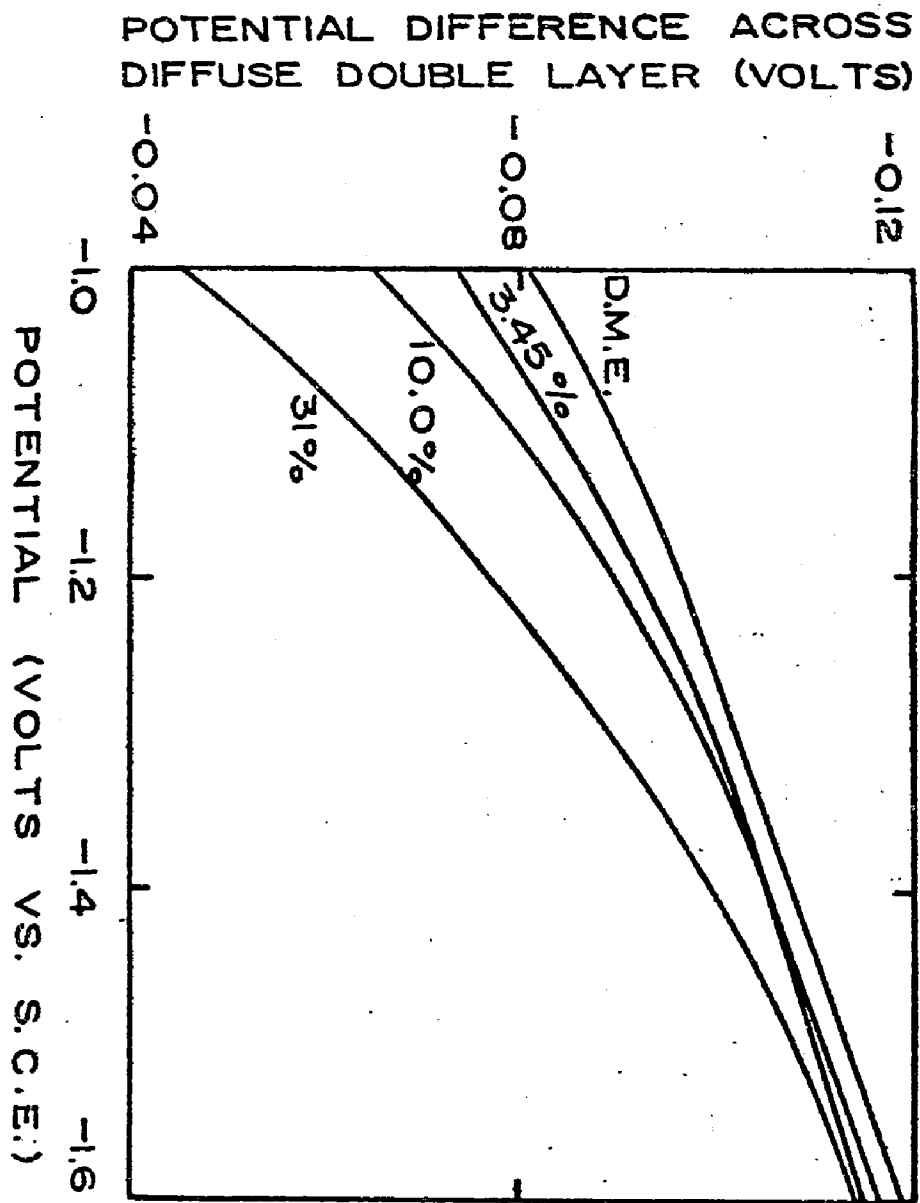


Fig. 11. $\phi_4 - \phi_s$ versus E for the dropping Hg and Tl amalgam electrodes in 0.1 M NaCN.

CHAPTER VIII

CONCLUSIONS

In the absence of specific adsorption and complexation the effect of foreign electrolytes on the kinetics of electrode reactions seems to be primarily due to variations in the structure of the double layer. Agreement between theory and experiment is good, especially for z-z electrolytes.

The effect of the nature of the electrode on simple processes without specific adsorption can be interpreted in the same manner as the salt effect. There are, however, more experimental limitations to the study of this variable. The difference $\phi_H - \phi_S$ cannot be varied over such a wide range as by change of the supporting electrolyte concentrations. Another difficulty, at least in this work, resulted from the greater uncertainty about differential capacities of the amalgam electrodes in comparison with the more reliable values for pure mercury. The abnormally high differential capacities obtained at the less negative potentials suggest a faradaic contribution, which may vitiate the value of the integral capacity K_1 , at least for potentials not very negative with respect to the electrocapillary maximum. This may explain why the quantitative agreement between theory and experiment is not as good as in the case of the salt effect (although the predicted trends are verified), apart from the fact that more

reliable values of the points of zero charge for the different electrodes require more extensive determinations than attempted in this work.

Limitations of the Theory.

The development of the theory of the double layer rests on a model which, at least qualitatively, explains many phenomena satisfactorily. Quantitatively, for the case of the salt effect of z-z electrolytes the range of concentrations in which the theory is valid is greater than the range in which the theory of Debye and Hückel holds. The theory has, however, some simplifying assumptions which cannot be entirely justified. It is assumed, for instance, that the diffuse double layer has a continuous structure. While this may be true for thicknesses of 10^{-6} cm. or greater, it is not so for thicknesses of about 10^{-7} cm. or less (since in this case we have only a few molecular or ionic layers) and these thicknesses are encountered with concentrations of inert electrolyte 10^{-1} M or higher. A rather important simplification of theory is the omission of consideration of ionic interactions in the double layer which could, among other things, promote ion-pair formation. In view of this limitation the agreement between theory and experiment appears sometimes to be too good.

Implications in Electrochemical Kinetics.

It was seen that the effective difference of potential

which favors and/or hinders the electrode reaction is obtained by subtracting from the experimental electrode potential the difference of potential between the plane of closest approach and solution. Hence, the latter must be controlled. This has not been generally done. Distortion of irreversible polarographic waves may occur because of change of double layer structure with potential. This is especially true in the vicinity of the point of zero charge (Fig. 2). It may therefore be desirable to minimize double layer effects. This can be done by using high concentrations of supporting electrolyte ($\approx 1M$ for 1:1 electrolytes).

Application of these ideas is suggested to the interpretation of the many empirical studies of the shift of half-wave potentials for irreversible polarographic waves upon addition of foreign electrolytes. In the discharge of certain metal ions it might be possible to separate the double layer effect from the influence of complexation upon addition of electrolyte.

SELECTED BIBLIOGRAPHY

- (1) A. N. Frumkin "Wasserstoffuberspannung und Struktur der Doppelschicht," Z. physik. Chem., A164, 121 (1933).
- (2) S. Lewina and U. Sarinsky, "Wasserstoffuberspannung an Quecksilber und das ζ Potential," Acta Physicochim U.R.S.S. 6, 491 (1937).
- (3) A. N. Frumkin and E. A. Aikazyan, "Bemerkung zur Theorie der Wasserstoffuberspannung," Doklady Akad. Nauk, S.S.S.R., 7, 475 (1937).
- (4) A. N. Frumkin and E. A. Aikazyan, "Ionization kinetics of molecular Hydrogen on a platinum electrode and the role of anions," Doklady Akad. Nauk, S.S.S.R., 100, 315 (1955).
- (5) A. N. Frumkin and G. M. Florianovich, "Electro-reduction of anions," Doklady Akad. Nauk, S.S.S.R., 80, 907 (1951). (Contains references to earlier work by Frumkin's school and others.)
- (6) V. S. Bagotskii and I. E. Yablokova, "Mechanism of electrochemical reduction of oxygen," Zhur. Fiz. Khim., 26, 1663 (1953).
- (7) A. N. Frumkin, "Symposium on Electrode Processes, Philadelphia, May 1959." E. Yeager, Editor, Wiley, New York, in course of publication.
- (8) L. Gierst, "Cinetique d'approche et reactions d'electrodes irreversibles," these d'agregation, University of Brussels, 1958.
- (9) L. Gierst, "Symposium on Electrode Processes, Philadelphia, May, 1959," E. Yeager, Editor, Wiley, New York, in course of publication.
- (10) M. Breiter, M. Kleinerman and P. Delahay, "Structure of the double layer and electrode processes," J. Am. Chem. Soc., 80, 5111 (1958).
- (11) J. A. V. Butler, Chapter II in "Electrical Phenomena at Interfaces," J. A. V. Butler, Editor, Methuen and Co., London: 1951, p. 64.

- (12) D. C. Grahame, "Electrical double layer and the theory of electrocapillarity," Chem. Revs. 41, 441 (1947).
- (13) Parsons, Chapter III in "Modern Aspects of Electrochemistry," J.O.M. Bockris, Editor, Butterworths Scientific Publications, London, 1954, pp. 103-179.
- (14) E. A. Guggenheim, "Thermodynamics," 3rd Ed., Interscience Publishers, Inc., New York, N.Y., 1957, pp. 410-416.
- (15) A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa and B. N. Kabanov, "Kinetics of Electrode Processes," Moscow, University Press, Moscow, 1951, p. 17.
- (16) T. Berzins and P. Delahay, "Kinetics of fast electrode reactions," J. Am. Chem. Soc., 77, 6448 (1955); see previous work of other investigators quoted therein.
- (17) V. G. Levich, "Theory of the non-equilibrium double layer," Doklady Akad. Nauk, S.S.S.R. 67, 309 (1949).
- (18) P. Delahay and T. Berzins, "Theory of electrolysis at constant current with partial or total control by diffusion. Application to the study of complex ions," J. Am. Chem. Soc., 75, 2468 (1953).
- (19) P. Ruetschi, "Polarographische Methode zur Bestimmung der Dissoziationsgeschwindigkeit von Sauren," Z. physik. Chem., N.F., 5, 323 (1955).
- (20) L. Gierst and H. Hurwitz, "Double layer corrections in the evaluation of rate and equilibrium constants of fast homogenous reactions —. Some potentialities of the galvanostatic method," International Colloquium on Fast Reactions in Solution, Hahnenklee-Harz (Germany) September, 1959.
- (21) H. Matsuda, "Double layer structure and electrode processes with a preceding chemical reaction," J. Am. Chem. Soc., in course of publication.
- (22) R. Parsons, "Symposium on Electrode Processes, Philadelphia, May, 1959," E. Yeager, Editor, Wiley, New York, in course of publication.
- (23) P. Delahay and C. C. Mattax, "Influence of foreign electrolytes and temperature in electrochemical kinetics. An application of polarography and voltammetry at constant current," J. Am. Chem. Soc., 76, 5314 (1954). See ref. therein for the polarography of iodate.

- (24) A. N. Frumkin and A. Gorodetszkaya, "Kapillarelekttrische Erscheinungen an Amalgamen, I. Thalliumamalgame," Zeit. Physik. Chem. A 136, 451 (1928).
- (25) E. F. Orlemann and T. M. Kolthoff, "Reduction of iodate and bromate at the dropping Hg electrode in neutral and basic media and the effect of salts on the current-voltage curves," J. Am. Chem. Soc. 64, 1970 (1942).
- (26) T. A. Krjukova, "Reduction of persulfate on a dropping mercury cathode and effect of the electric field of the surface charges of the electrode on the course of electrochemical reactions," Doklady Akad. Nauk, S.S.S.R. 54, 517 (1949).
- (27) K. Koutecky, "Theorie langsamer Elektrodenreaktionen in der Polarographie und polarographisches Verhalten eines Systems bei welchem der Depolarisator durch eine schnelle chemische Reaktion aus einen elektroinaktiven Stoff entsteht," Collection Czechoslovak Chem. Commun. 18, 597 (1953).
- (28) J. E. Randles and K. W. Sommerton, "Kinetics of rapid electrode reactions, III--Electron-exchange reactions," Trans. Faraday Soc., 48, 957 (1952).
- (29) L. Gierst and A. Juliard, "Etude oscillographique des regimes transitoires de diffusion," Proc. Intern. Comm. Thermodynam. and Kinet., 2nd meeting, Tamburini, Milan, 1950, p. 117.
"Non-steady state electrolysis under constant forced currents," J. Phys. Chem. 57, 701 (1953).
- (30) H. Gerischer, "Die Geschwindigkeit der Reaktion," $\text{Cd}(\text{CN})_4^{2-} \text{aq} \rightleftharpoons \text{Cd}(\text{CN})_3^- \text{aq} + \text{CN}^- \text{aq}$. Z. physik. Chem., N.F., 2, 79 (1954).
- (31) J. Koryta, "Kinetic der polarographischen Reduktion von Kadmiumcyanidkomplexen," Z. Elektrochem., 61, 423 (1957).
- (32) L. Gierst, "Unterscheidung der verschiedenen Elektrodenmechanismen durch Messung der Übergangszeit bei konstantem Strom in ruhender Lösung," ibid., 59, 784 (1955).

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